Anal. Calcd for $C_8H_{10}N_2O$: C, 63.97; H, 6.72; N, 18.66. Found: C, 64.12; H, 6.71; N, 18.80.

Reaction of 1 with Benzenethiol.—To a solution of 0.05 g (0.0022 g-atom) of sodium in 20 ml of absolute ethanol was added 3.3 g (0.03 mol) of benzenethiol and then 4.5 g (0.025 mol) of **1**, and the mixture was heated at reflux for 7 hr under argon. The ethanol was distilled under reduced pressure, and an ether solution of the residue was washed three times with water and once with saturated sodium chloride solution and dried ($CaCl_2$). Concentration under reduced pressure left 4.5 g of crude product which was distilled to give 3.5 g (48%) of colorless liquid (ethyl 2-cyano-3-methyl-6-phenylthio-2-hexenoate): bp 167–168° (0.2 mm); $n^{25}D$ 1.5558; near-ir $\lambda_{max}^{CCl_4}$ 1.72 (s), 1.79 (m), 2.18 (s), 2.29 (s), 2.33 (s), 2.38 (m), 2.44 (m), 2.50 (s) μ; ir $\lambda_{max}^{CCl_4}$ 4.5 (m, C≡N), 5.76 (s, ester C=O), 6.21 (s, C=C), 13.6 and 14.5 (s, C_6H_5) μ; nmr ($CDCl_3$) δ 7.25 (m, 5, C_6H_5), 4.22 (q, 2, OCH_2CH_3), 2.78 (m, 4, $SCH_2CH_2CH_2C$=C), 2.17 and 2.27 (each a singlet, *cis*- and *trans*-CH_3—C=C—), 1.86 (m, 2, $SCH_2CH_2CH_2C$=C), and 1.28 ppm (t, 3, OCH_2CH_3).

Anal. Calcd for $C_{16}N_{19}NSO_2$: C, 66.39; H, 6.63; N, 4.84. round: C, 66.28; H, 6.71; N, 4.88.

Reaction of 1 with 1-Butanethiol.—The reaction was carried out as described for thiophenol, using 2.75 g of 1-butanethiol. Final distillation gave 2.2 g of colorless liquid ethyl 2-cyano-3-methyl-6-butylthio-2-hexenoate: bp 142–143° (0.2 mm); $n^{25}D$ 1.4992.

Anal. Calcd for $C_{14}H_{23}NO_2S$: C, 63.36; H, 8.73. Found: C, 63.19; H, 8.50.

Both infrared and near-infrared spectra showed absorptions similar to the thiophenol product except for the absence of peaks due to the aromatic ring.

Reaction of 2 with Secondary Amines. Formation of Dimer.—A secondary amine (0.022 mol) was added at a fast rate dropwise to a solution of 2 g (0.015 mol) of **2** in 10–15 ml of absolute ethanol. Dimethylamine, diethylamine, or piperidine were used. A reaction occurred immediately, and after 1 hr, concentration under reduced pressure left a thick red oil which crystallized to a large extent after standing in the refrigerator for several days. Recrystallization (50% ethanol) gave yields of 0.5–1.3 g of light yellow crystals, mp 115–116°. A final recrystallization for an analytical sample was best accomplished from heptane: mol wt, calcd 264, found (benzene) 278; ir $\lambda_{max}^{CHCl_3}$ 2.88 (w, NH_2), 2.96 (m, NH_2), 4.55 (m, conjd C≡N), 6.1–6.16 (s), 6.34 (m, conjd C=C), 9.75 (m, broad, cyclopropyl), and 10.82 μ (w, broad, —C=C—H); nmr ($CHCl_3$) δ 5.71 (s, broad, 2, $-NH_2$), 4.62 and 4.65 [two singlets due to geometric isomers, 1, $-(NH_2)CH$=C], 1.23 (s, 3, CH_3—C=C), and 0.2–1.66 ppm (m, 10, two cyclopropyl).

Anal. Calcd for $C_{16}H_{16}N_4$: C, 72.69; H, 6.11; N, 21.20. Found: C, 72.91; H, 6.02; N, 21.37.

Transesterification of 1 with 1-Butanol in the Presence of Amines.—Diethylamine, piperidine, and morpholine all catalyzed this reaction to give the same single product in yields ranging from 32% for morpholine to 59% for the other two. The amine (0.048 mol) was dissolved in 20 ml of 1-butanol and added dropwise to a refluxing solution of 7.1 g (0.04 mol) of **1** in 30 ml of 1-butanol. The mixture was heated at reflux for an additional 2 hr and concentrated under reduced pressure, and the residue was distilled to give a colorless oil, *n*-butyl 2-cyano-3-cyclopropyl-2-butenoate: bp 109–110° (0.1 mm); $n^{25}D$ 1.5022.

Anal. Calcd for $C_{12}H_{17}NO_2$: C, 69.52; H, 8.28; N, 6.76. Found: C, 69.34; H, 8.41; N, 6.90.

The same transesterification could be effected by use of Triton B (ratio, 17 mol of compound **1**/1 mole Triton B) in 22% yield.

Registry No.—**1** (solid), 17407-28-2; **1** (liquid), 17407-29-3; **2**, 17407-30-6; dimer of **2**, 17407-31-7; **3**, 17407-32-8; $C_{16}H_{19}NSO_2$ (*cis*), 17407-33-9; $C_{16}H_{19}NSO_2$ (*trans*), 17407-34-0; $C_{14}H_{23}NO_2S$, 17407-35-1; $C_{12}H_{17}NO_2$, 17407-36-2.

Acknowledgment.—This research was supported in part by a grant from the Petroleum Research Fund of the American Chemical Society. Grateful acknowledgment is made to the donors of this fund. We are also grateful to Dr. Graeme Baker of Montana State University, Bozeman, Mont., fors ome of the nmr spectra.

Isomerization of Terpenes. The Isomerization of (−)-Perillaldehyde to *p*-Mentha-1,3-dien-7-al with Aqueous Sulfuric Acid

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Received June 26, 1968

Isomerization of some terpenoid compounds with aqueous acid or alkali has been observed by several workers. (−)-Perillaldehyde (**1**), however, has not yet been included in these investigations.

In the present paper, a monoterpene $\alpha\beta,\gamma\delta$-dienal, *p*-mentha-1,3-dien-7-al (**2**), was obtained from **1** on treatment with aqueous sulfuric acid. The same dienal structure as **2** has been assigned by Goryaev[1] to an oxidation product of sabinene with selenic acid and also by Matsuura[2] to one of the oxidation products of α-terpinene with *t*-butyl chromate, independently.

The apparent discrepancies in physical properties,[1,2] however, were found between the present authors' data and those by Matsuura and Goryaev. Based on the evidence to be presented below, it may be concluded that acid-catalyzed isomerization product of (−)-perillaldehyde is a monoterpene aldehyde, *p*-mentha-1,3-dien-7-al, different from the products described by Matsuura and Goryaev.

The isomerization of **1** was conducted in 10% aqueous sulfuric acid at 120–130° for 3 hr and afforded **2** in a 90% yield.

The absorption bands at 1666, 2700, and 2800 cm^{-1} in the ir spectrum of **2** are attributable to $\alpha\beta,\gamma\delta$-unsaturated aldehyde.[3-5]

In general, as the number of double bonds in conjugation increases, the C=C vibration tends to shift progressively toward lower frequencies and enhance the intensity,[6] so that the strong absorption at 1570 cm^{-1} is reasonably attributed to $\alpha\beta,\gamma\delta$ double bond conjugated with carbonyl group. Matsuura, however, has reported no absorption band in this region.

In addition to the ir data, the spectral assignment of these chromophores is demonstrated by the maximum absorption at 315 mμ (ϵ 15,600) which is comparable with the accepted absorption maximum at 320 mμ for the conjugated dienone system according to the Fieser rule. The absorption maximum and intensity at 305 mμ (ϵ 4500) of the compound reported by Matsuura are not only inconsistent with the authors', but also lower than the values to be expected from the structure **2**.

Further evidence to support the structure of **2** was

(1) M. I. Goryaev and G. A. Tolstikov [*Izv. Akad. Nauk SSSR, Ser. Khim.*, 72 (1962)] reported that the physical constants of the product were 2,4-DNPH mp 181–182° and semicarbazone mp 201–202°.

(2) T. Matsuura and T. Suga [*J. Org. Chem.*, **30**, 518 (1965)] reported that the physical constants of the product were ν_{max} 2750, 1670, 1375, 1357 cm^{-1}; λ_{max}^{MeOH} 305 mμ (ϵ 4500); 2,4-DNPH mp 230–231°, λ_{max}^{MeOH} 405 mμ (ϵ 28,000).

(3) A. Pozefsky and N. D. Coggeshall, *Anal. Chem.*, **23**, 1611 (1951).

(4) A. Ashdown and T. A. Kletz, *J. Chem. Soc.*, 1454 (1948).

(5) R. B. Turner and D. M. Voitle, *J. Amer. Chem. Soc.*, **73**, 1403 (1951).

(6) R. N. Jones, P. Humphries, E. Packard, and K. Dobriner, *ibid.*, **72**, 86 (1950).

provided by the nmr spectrum (CCl_4). The methyl protons of the isopropyl group afford doublets at δ 0.99 and 1.10 ppm,[7] and the sharp band at δ 9.40 ppm unequivocally shows the presence of a CHO group carrying no α hydrogen. The line at δ 2.25 ppm consisting of four protons is assigned to CH_2 group in the ring. The signal at δ 5.92 and 6.68 ppm (each doublet J = 6 cps) can be assigned to vinyl protons of β and γ positions, respectively.

Compound 2 may be of synthetic interest from the viewpoint of its possessing the possibility of further transformations and it is fascinating that the compound can be obtained quantitatively by a simple procedure.

Experimental Section[8]

Acid Treatment on (−)-Perillaldehyde.—A mixture of (−)-perillaldehyde (10 g) and 10% aqueous sulfuric acid (150 ml) was refluxed for 3 hr at 120–130°; then the resulting solution was extracted with ether. The ether solution was neutralized, washed with water, dried over anhydrous sodium sulfate, and distilled *in vacuo* to give 9 g of 2, bp 81–82° (6 mm), in a 90% yield: d^{20}_4 0.9795; $n^{20}D$ 1.5283, MD 47.18° (calcd 45.06°); ν_{max} 2700, 2800, 1666 (CHO), 1570 ($\alpha\beta,\gamma\delta$-conjugated diene), 1360, 1380 (isopropyl), 780, 840 cm^{-1} (double bond); λ^{MeOH}_{max} 315 mμ (ϵ 15,600); δ 0.99, 1.10 (d, 6 H), 9.40 (s, 1 H), 2.25 (s, 4 H), 5.92, 6.68 ppm (each doublet J = 6 cps, 2 H); semicarbazone mp 193–194°.

Anal. Calcd for $C_{11}H_{17}ON_3$: C, 63.74; H, 8.27; N, 20.27. Found: C, 63.95; H, 8.49; N, 20.21.

Registry No.—1, 18031-40-8; 2, 1197-15-5; semicarbazone of 2, 18039-53-7; sulfuric acid, 7664-93-9.

Acknowledgments.—The authors are indebted to Dr. Yuzo Inouye, Institute for Chemical Research, Kyoto University, for his kind advice and suggestions. They also wish to express their thanks to Japan Electron Optic Laboratory Co., Ltd., for nmr analysis.

(7) S. K. Paknikar and S. C. Bhattacharyya, *Tetrahedron*, **18**, 1509 (1962).

(8) All melting and boiling points are uncorrected. Microanalysis was performed on a Yanagimoto CHN-corder. Ir spectrum was obtained with a Hitachi EPI-2 spectrophotometer using sodium chloride liquid film cell. Uv spectrum was obtained with a Hitachi EPS-3 recording spectrophotometer in methanol solution. The nmr spectrum has obtained with Japan nuclear magnetic resonance spectrum spectrophotometer JNM-4 H-100 in carbon tetrachloride contained tetramethylsilane (TMS) as an internal reference. Chemical shifts are expressed in δ values (parts per million) from TMS.

Reaction of *gem*-Dibromocyclopropanes with Morpholine

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Received March 22, 1968

The reaction of *gem*-dihalocyclopropanes with electrophilic or nucleophilic reagents is a useful method of extending the carbon chain of olefins and leads to several otherwise difficultly accessible molecules.[2] In a previous paper[2] it was shown that a variety of electrophilic reagents readily react with *gem*-dihalocyclopropanes to yield allyl derivatives or dienes. Since no data exists in the literature on the reaction of basic nitrogen compounds with *gem*-dibromocyclopropanes to give N-substitution products, it was of interest to investigate the reaction of morpholine in the above reaction.

The results of this investigation indicate that refluxing a morpholine solution of substituted *gem*-dibromocyclopropane for 1–154 hr yields β-bromoallylmorpholines or the 3-bromo-1,3-diene as described in Tables I and II. The thermal ring opening of the neat *gem*-dibromocyclopropanes yielded in some cases isolable β-bromoallyl bromides or the 3-bromo-1,3-diene.

This ring-opening reaction takes place readily with the more highly alkylated *gem*-dibromocyclopropanes and follows the same order of reactivity observed with electrophilic reagents.[2] In the case of 1,1-dibromo-2,2,3,3-tetramethylcyclopropane (VII), 3-bromo-2,4-dimethyl-1,3-pentadiene (VIII) is obtained in 82% yield even in the absence of any solvent by heating to 160–162° for 2.5 hr. The reaction of 1,1-dibromo-2,2-dimethylcyclopropane (I) with morpholine yielded 3-bromo-2-methyl-4-morpholino-2-butene (II), whereas in the absence of morpholine 1,2-dibromo-3-methyl-2-butene (III) was obtained. The thermal ring opening of other neat *gem*-dibromocyclopropanes does not always lead to the isolation of clearly defined products.

Attempts to thermally rearrange the *cis*- and *trans*-butene-2-dibromocarbene adducts in the absence of solvent yielded tars. However, carrying out the same reaction in refluxing morpholine gave an immediate precipitation of morpholine hydrobromide from the *cis* adduct. The *trans* adduct gave a similar precipitation after a longer period of refluxing. Both *cis*- and *trans*-butene-2-dibromocarbene adducts yielded the same isomeric product (V) as shown by analysis using gas–liquid partition chromatography (glpc) and infrared (ir) and nuclear magnetic resonance (nmr) spectroscopy.

Recently[2] it was reported that these same *cis*- and *trans*-dibromocarbene adducts also yield one isomeric product upon reaction with aqueous silver nitrate or silver acetate–acetic acid.

In the case of *cis*- and *trans*-1,1-dibromo-2,3-dimethylcyclopropane the transition states obtained by the favored disrotatory process[3-5] can be formulated as shown in Scheme I, p 4539.

In agreement with the above predictions it is found that *cis*-dimethyl isomer reacts faster than the *trans* isomer. This has also been reported to be true for the *cis* and *trans* isomers of 1,1-dichloro-2-methyl-3-ethoxycyclopropane.[6] In the latter case the *cis* and *trans* isomers also undergo a ring-opening reaction in

(1) (a) The Borden Chemical Co., Central Research Laboratory, Philadelphia, Pa. 19124. (b) This research was described in part in the Ph.D. Thesis of S. R. S., The Pennsylvania State University, University Park, Pa. 1960.

(2) S. R. Sandler, *J. Org. Chem.*, **32**, 3876 (1967), and references cited therein.

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(5) P. von R. Schleyer G. W. Van Dine, U. Schollkopf, and J. Paust, *ibid.*, **88**, 2868 (1966).

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